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Preparation of Poly(lactic acid) and Poly(trimethylene terephthalate) Blend Fibers for Textile Application

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Abstract

Biodegradable poly(lactic acid) (PLA) and poly(trimethylene terephthalate) (PTT) blend fibers were prepared in this study. PLA and PTT were blended in a twin screw extruder with varied contents of PTT 0-50 wt%.The PLA/PTT blend were melt spun into fiber by melt spinning technique. Thermal properties and crystallization behavior of PLA/PTT blends were investigated. PLA fiber was glossy and transparent while PTT fiber was opaque. The spinning of PLA/PTT blends fiber was difficult due to the difference in melting characteristic of PLA and PTT. However, the PLA/PTT blend fiber was successfully spun at PTT content of 10 wt% with the barrel temperature of 250 °C and would be suitable for textile application.

Selection and peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

Keywords: poly(lactic acid), poly(butylene succinate), melt spinning, miscibility, crystallinity

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1. Introduction

Plastic materials are widely applied for various kinds of industries due to their high specific strength and light weight. However, general plastic materials have been synthesized from petrochemical resources, which now are running out and make the environmental problems due to their non biodegradability. Therefore, in the present day, biodegradable plastics are promising benefited for environmental friendly materials. Poly(lactic acid) (PLA) is now available and has been an attractive biodegradable plastic. It exhibits high strength, clarity and biodegradability. However, PLA is brittle, which is a limitation for appling in textile industry. For improving the ductility and flexibility of PLA, it has been adding with plasticizers such as polyethylene glycol or triacetine [1-2] or blending with polymers such as biodegradable polyester i.e. poly(butylene succinate) (PBS), poly(butylene succinate-co-adipate) (PBSA) or natural rubber [3-6].

PLA fiber is great interested for biological and medical application, which was reviewed by Gupta et al [7]. Du et al [8] studied on structure and properties of commercial PLA fiber producing in China, which their results were useful for further applied PLA fiber in the industries. Sawada et al [9] modified PLA fiber with enzymatic treatment. They summarized that the enzymatic treatment caused the hydrolysis of PLA fiber resulting in the reduction in fiber strength. Reddy et al [10] prepared PLA and polypropylene (PP) blend fibers in order to improve the biodegradability, dyeability and resistance to hydrolysis. PLA in PLA/PP blends fiber had better resistance to hydrolysis and dyeable with disperse dyes. However, there is still less information about PLA blends fiber for development in textile application.

Poly(trimethylene terephthalate) (PTT) is an aliphatic polyester, which is synthesized from 1,3-propanediol that derived from renewable resources such as corn sugar [11]. PTT has been widely used in textile applications. Their properties exhibit superior strength and excellent dyeablitity [12-14]. Blending PLA with PTT would develop a new material for textile applications.

In this research, PLA and PTT blends fibers were prepared by melt spinning process. Thermal properties and crystallization behavior of PLA:PTT blends fiber were investigated upon the effect of PLA:PTT blend ratio. Mechanical properties of the blends were elucidated from compression molded specimens.

2. Experimental

2.1 Materials and fabrication

Poly(lactic acid) (PLA) (Grade 3051D) was supplied by NatureWorks LLC, USA. The melt fow rate was 10-30 g/10 min. Poly(trimethylene terephthalate) (PTT) was purchased from the company in China. The melt flow rate was 20 g/10 min. The ratios between PLA:PTT blends were varied from 90:10, 80:20, 70:30, 60:40 and 50:50. The neat PLA and PTT were also prepared as controlled. Table 1 tabulates the composition of PLA and PTT in the blends and the sample designation.

Table 1. PLA/PTT Blend compositions.

PLA contents (wt%)	PTT contents (wt%)	PLA:PTT Sample designation
100	0	PLA
90	10	PLA90:10PTT
80	20	PLA80:20PTT
70	30	PLA70:30PTT
60	40	PLA60:40PTT
50	50	PLA50:50PTT
0	100	PTT

PLA and PTT were dried in an ovent at 80 °C for at least 8 hours before compounding in a twin screw extruder (KEDSE 20/40, Brabender, Germany). The barrel temperature was set at 190-250 °C with a screw speed of 80 rpm. After pelletized, PLA:PTT blends were dried before fiber preparation. PLA, PTT and their blends were melt-spun by a single screw extruder (ThermoHaake, Germany) equipped with multifilament spinneretes. The barrel temperature was set at 200-250 °C with a screw speed of 50 rpm.

Neat polymer and the PLA:PTT blends were compression moled at temperature set of 250 °C for mechanical properties investigation.

2.2. Characterization

Thermal properties and crystallization behavior of PLA, PTT and the blends were investigated by a differential scanning calorimeter (NETZSCH, DSC 200 F3) at temperature range of 30-270 °C at a heating and a cooling rate of 10 °C/min under nitrogen atmosphere. The DSC melting and cooling thermograms were recorded for analysis. The crystallinity of polymer was calculated from the following equation.

$$\%X_c = \frac{\Delta H_f \times 100}{\Delta H_{f100}} \tag{1}$$

Where X_c = Degree of crystallinity
ΔH_f = Heat of fusion of polymer
ΔH_{f100} = Heat of fusion of 100% polymer Crystallization

ΔH_{f100} of PLA was 93 J/g [15] and ΔH_{f100} of PTT was 104 J/g [16].

Tensile properties of the compression moled specimens were carried out according to ASTM D638 by an Instron universal testing machine (Instron5560). The extension rate was 10 mm/min.

3. Results and Discussion

3.1. Thermal Properties of PLA/PTT Blends

Fig. 1 and 2 depict DSC results of melting and cooling thermograms of neat PLA, neat PTT and PLA:PTT blends, respectively. The melting curve of PLA exhibited three steps changing including the step of glass transition temperature (T_g) of PLA at around 62.8 °C followed by the exothermic peak of cold crystallization (T_{cold}) around 122 °C and the melting temperature (T_m) peak of PLA at 152.6 °C. The cold crystallization appeared in PLA melting thermogram indicated that PLA was difficult to crystallize hence the crystallization was occurred during the melting process [17]. On the other hand, the DSC thermogram of PTT showed three steps of changing including the step of T_g at 46.2 °C, exothermic peak of T_{cold} at around 60 °C and T_m peak of PTT at 230 °C. The cold crystallization of PTT was corresponded to melt-quench of PTT [18]. The heating thermograms of PLA:PTT blends exhibited the step of changing with both PLA and PTT in the blends. Two melting temperatures in the heating thermograms of the blends were related to the melting characteristic of PLA and PTT, which indicated that PLA and PTT were immiscible. However, intensities of melting peaks of PLA and PTT in the blends were decreased depend on the PLA and PTT compositions in the blends.

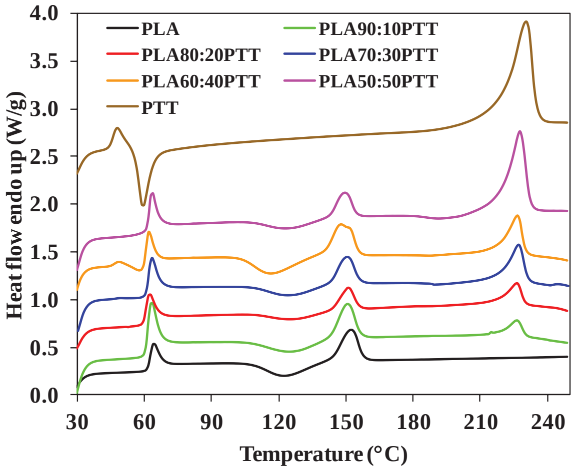

Fig. 1. DSC melting thermograms of PLA, PTT and their blends.

Fig. 2 illustrates DSC cooling thermograms of neat polymers and the blends, which represented to crystallization temperature (T_c) of the polymer. There was no T_c in the PLA thermogram, which indicated that PLA was difficult to crystallize. PTT cooling peak of T_c is clearly seen at temperature around 184 °C. Blending PLA with PTT would promote crystallization of PLA, which indicated by the exothermic peak of PLA crystallization in the blends at around 90-95 °C as shown in Fig. 2 The peak intensity of PLA can be clearly seen when blending with PTT 10-30 wt% then the intensity decreased when adding PTT at higher contents. On the contrary, the peak intensity of PTT decreased when blending with PLA. It was attributed to PTT would act as a nucleating site for PLA crystallization while PLA retarded the crystallization of PTT. Therefore, in the blends, PLA crystallinity would be enhanced where as PTT crystallinity was diminished [19].

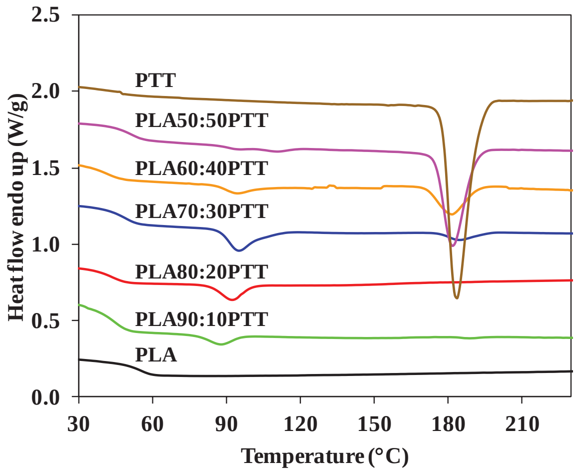

Fig. 2. DSC cooling thermograms of PLA, PTT and their blends.

Thermal properties and the crystallinity of neat polymers and the blends are tabulated in Table 2. T_m values of both PLA and PTT in the blends decreased when increasing either PTT or PLA fraction in the blends. The declination of T_m was due to decreasing of crystal size of PLA or PTT in the blends [20]. From the results, T_c of PLA in the blends increased when increasing PTT contents. Likewise, T_c of PTT in the blends also increased at a lower PLA contents. It was due to PTT would enhance crystallization of PLA, which resulting in increasing PLA crystallinity. However, PLA might hinder PTT crystallization, which resulting in the reduction of PTT crystallinity.

Table 2. Thermal properties of PLA, PTT and their blends.

Samples	PLA			PTT		
	T_m (°C)	T_c (°C)	$\%X_c$	T_m (°C)	T_c (°C)	$\%X_c$
PLA	152.6	-	18.2	-	-	-
90:10	151.0	88.0	19.5	226.6	189.1	7.8
80:20	151.4	92.7	21.9	226.5	186.0	11.7
70:30	150.5	95.3	20.6	227.1	185.3	23.8
60:40	148.1	94.7	22.9	226.9	182.1	26.2
50:50	149.7	95.7	13.4	227.9	182.0	51.0
PTT	-	-	-	230.7	183.7	80.9

3.2. PLA/PTT blends fiber

PLA, PTT and their blends fibers were melt-spun by melt spinning process. The melt spinning of the blends fiber was difficult due to the difference on the melting characteristic of PLA and PTT. The processing temperature was set up at 250 °C for melting PTT while PLA was degraded at this temperature. Figure 5 shows photographs of melt-spun PLA, PTT and the blend fibers. PLA fiber was clear, glassy and brittle while PTT fiber was opaque and soft. The PLA/PTT blends fibers were not smooth, which was attributed to the immiscibility of PLA and PTT in the blends. It can be noted that PLA:PTT blend fiber was successfully spun at PTT content of 10 wt%.

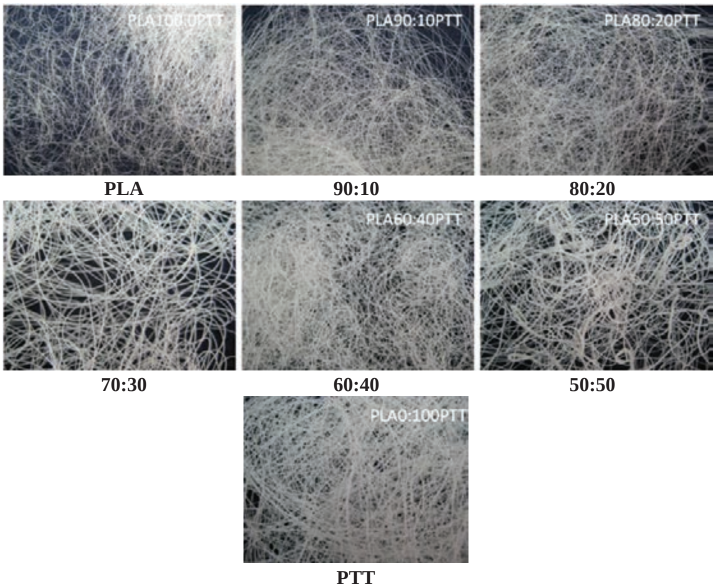

Fig.3 Photographs of PLA, PTT and their blends fibers.

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3.3. Mechanical properties of PLA/PTT blends

Mechanical properties of PLA, PTT and their blends are presented in Fig. 4 and 5 for tensile modulus and tensile strength, respectively. PTT exhibited the highest tensile modulus at 1.4 GPa while tensile modulus of PLA was around 1.0 GPa as shown in Fig. 4. Tensile modulus of the blends increased with increasing PTT contents, which was due to the stiffness of PTT. However, the tensile modul of PLA:PTT blends were low due to degradation of PLA when fabricated the blends at the processing temperature of 250 °C. Tensile strength of the blends slightly increased when increasing PTT contents in the blends as shown in Fig. 5. However, tensile strength of the blends was low, which due to the PLA degradation and an immiscibility between PLA and PTT in the blends.

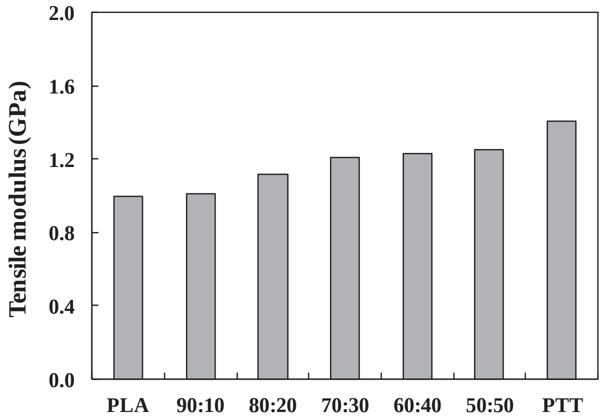

Fig. 4 Tensile modulus of PLA, PTT and their blends.

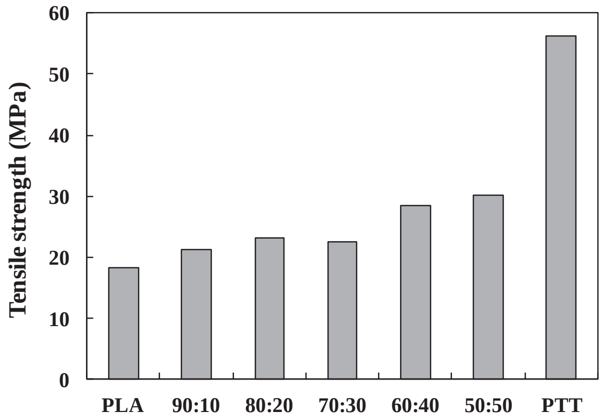

Fig. 5 Tensile strength of PLA, PTT and their blends

4. Conclusions

Thermal properties and crystallization behavior of PLA:PTT blends fibers were clarified in this study. The incorporation of PTT enhanced crystallization of PLA in PLA:PTT blends, which then improve crystallinity of PLA in the blends. The melting characteristic of PLA and PTT in the blends was an important factor in order to selecting processing temperature for spinning PLA/PTT blend fiber. In this study, the PLA/PTT blend at 90/10 ratio could be melt-spun into fibers at the barrel temperature of 250 °C. It can be noted that tensile properties of the PLA/PTT blends increased when increasing PTT contents, which also would apply PLA/PTT blends fiber for textile industry.

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References

[1] Li H and Huneault MA. Effect of nucleation and plasticization on the crystallization of poly(lactic acid). *Polymer*, 2007; **48**: 6855-6866.

[2] Ljungberg N, Andersson T and Wesslen B. Film extrusion and film weldability of poly(lactic acid) plasticized with triactin and tributyl citrate. *J Appl Polym Sci.*, 2003; **88**: 3239-3247.

[3] Harada M, Ohy T, Iida K, Hayashi H, Hirano K and Fukuda H. Increased impact strength of biodegradable poly(lactic acid)/poly(butylene succinate) blend composites by using isocyanate as a reactive processing agent. *J Appl Polym Sci.*, 2007; **106**:1813-1820.

[4] Wang R, Wang S and Zhang Y. Morphology, rheological behaviour, and thermal stability of PLA/PBS/POSS composites. *J Appl Polym Sci.*, 2009; **113**: 3095-3102.

[5] Signori F, Coltelli MB and Bronco S. Thermal degradation of poly(lactic acid) (PLA) and poly(butylenes adipate-c0-terephthalate) (PBAT) and their blends upon melt processing. *Polym Degrad Stab.*, 2009; **94**: 74-82.

[6] Bitinis N, Verdejo R, Cassagnau P and Lopez-Manchado MA. Structure and properties of polylactide/natural rubber blends. *Mater Chem Phys.*, 2011; **129**: 823-831.

[7] Gupta B, Revagade N and Hilborn J. Poly(lactic acid) fiber: An overview. *Prog Polym Sci.*, 2007; **32**: 455-482.

[8] Du Z, Xu Y and Yu W. Characterization of structure and properties of polylactic fiber. *J Appl Polym Sci.*, 2012; **125**: E149-E157.

[9] Sawada K, Urakawa H and Ueda M. Modification of polylactic acid fiber with enzymatic treatment. *Text. Res. J.*, 2007; **77**: 901-905.

[10] Reddy N, Nama D and Yang Y. Polylactic acid/polypropylene polyblend fibers for better resistance to degradation. *Polym Degrad Stab.*, 2008; **93**: 233-241.

[11] Kurian JV. A new polymer platform for the future-Sorona® from corn derived 1,3-propanediol. *J Polym Environ.*, 2005; **13**: 159-167.

[12] Chuah HH. Orientation and structure development in poly(trimethylene terephthalate) tensile drawing. *Macromolecules*, 2001; **34**:6985-6993.

[13] Lyoo WS. *et. al.* Effect of zone drawing on the structure and properties of melt-spun poly(trimethylene terephthalate) fiber. *J. Appl Polym Sci*, 2001; **81**: 3471-3480.

[14] Abe T, Azuma Y and Matsuo T. Poly(trimethylene terephthalate) fiber. U.S. Patent 6,495,254, 2002.

[15] Martin O and Avérous L. Poly(lactic acid): plasticization and properties of biodegradable multiphase system. *Polymer*, 2001; **42**: 6209-6219.

[16] Zhang J. Study of poly(trimethylene terephthalate) as an engineering thermoplastics. *J Appl Polym Sci.*, 2004; **91**:1657-1666.

[17] Wu D, Wu L, Wu L, Xu B, Zhang Y and Zhang M. Nonisthermal cold crystallization behaviour and kinetics of polylactide/clay nanocomposites. *J Polym Sci Part B.*, 2007; **45**:1100-1113.

[18] Chen Z, Luo J and Yan S. Crystal structure and thermal behaviour of cold-crystallized poly(trimethylene terephthalate). *Colloid Polym Sci.*, 2012; DOI 10.1007/s00396-012-2786-8, 1-10.

[19] Huang JW, Hung YC, Wen Y-L, Kang C-C and Yeh M-Y. Polylactide/nano- and micro-scale silica composite film. II. Melting behaviour and cold crystallization. *J Appl Polym. Sci.*, 2009; **112**: 3149-3156.

[20] Fornes TD and Paul DR. Crystallization behaviour of nylon 6 nanocomposites. *Polymer*, 2003; **44**: 3945-3961.